

Quasiparticle calculations of the electronic properties of ZrO_2 and HfO_2 polymorphs and their interface with Si

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(Dated: December 10, 2009)

Quasiparticle calculations are performed to investigate the electronic band structures of various polymorphs of Hf and Zr oxides. The corrections with respect to density-functional-theory results are found to depend only weakly on the crystal structure. Based on these bulk calculations as well as those for bulk Si, the effect of quasiparticle corrections is also investigated for the band offsets at the interface between these oxides and Si assuming that the lineup of the potential at the interface is reproduced correctly within density-functional theory. On the one hand, the valence band offsets are practically unchanged with a correction of a few tenths of eV. On the other hand, conduction band offsets are raised by 1.3–1.5 eV. When applied to existing calculations for the offsets at the density-functional-theory level, our quasiparticle corrections provide results in good agreement with the experiment.

PACS numbers: 71.10.-w, 73.40.Ty, 73.40.Lq, 85.40.-e, 85.60.-q

I. INTRODUCTION

In the microelectronic industry, the continuous quest for devices with improved performance and lower power consumption has recently stimulated an intense research on dielectric materials. Indeed, for over three decades, SiO_2 has formed the perfect gate dielectric material for metal oxide semiconductor field effect transistors (MOSFETs). However, fundamental limits have recently been reached that impede further downscaling of MOSFETs based on SiO_2 .¹ Candidate materials to substitute the latter are transition metal oxides and silicates with an high dielectric constant, specifically higher than SiO_2 , and are commonly referred to as *high-k* dielectrics. In this framework, ZrO_2 and HfO_2 , and more generally Zr and Hf compounds, have attracted considerable attention,¹ hafnium-based microprocessors being now in development or even already in production.²

Ab-initio calculations can nicely complement the experimental work to investigate the properties of these novel materials (see, e.g., Refs. 3,4,5) and to engineer the interfaces.^{6,7} The method of choice for investigating ground-state properties is density-functional theory (DFT) that allows to treat quite large systems on the one hand, and to obtain reliable results on the other hand.⁸ For the Si/ ZrO_2 and Si/ HfO_2 interfaces, various models have been explored using DFT.^{9,10,11,12,14,15,16} It was found that due to their analogous electronic structure, the two transition metal oxides present a very similar interfacial bonding. Moreover, there is general agreement that the O-terminated interfaces are more stable than metal-terminated ones.

One of the most stringent criteria in the design of Si/oxide interfaces is their band offsets (BOs) that control the transport properties, and hence the leakage current.¹ In particular, both the valence and conduction band offsets (VBO and CBO) should be larger than 1 eV

to obtain a low leakage. DFT relying on local or semilocal approximations for the exchange–correlation potential does not guarantee quantitatively correct BOs since the DFT eigenenergies do not correspond to the quasiparticle (QP) energies.^{17,18,19,20,21} However, the VBOs are often found with an accuracy of a few tenths of eV, especially for semiconductor interfaces.²² Therefore, the CBOs can also be predicted using a simple scissor operator to correct the band gaps to their experimental values. Several works have addressed the BOs at the Si/ ZrO_2 and Si/ HfO_2 interfaces using this scissor-corrected DFT scheme.^{9,10,11,12,13} The calculated VBOs for the stable insulating O-terminated interfaces of Si/ ZrO_2 and Si/ HfO_2 are around 2.5–3 eV, in reasonable agreement with the experiments (2.7–3.4 eV).^{23,24,25,26,27,28,29,30,31} The scissor-corrected CBOs are about 1.7–2.2 eV, and compare quite well with the experimental values (1.5–2 eV).^{28,29,30,31}

In contrast with DFT, the many-body perturbation theory (MBPT) within the *GW* approximation has proven to be a practical and sufficiently accurate method for calculating QP energies.^{32,33,34} In this method, the DFT eigenenergies within the local density approximation (LDA) or the generalized gradient approximation (GGA) level are corrected perturbatively (QP corrections) to obtain the QP energies. For semiconductor interfaces, the QP corrections on the band edges are often similar on both sides³⁵ and do not substantially affect the VBOs, explaining the success of DFT.²² Nevertheless, this approach cannot be generalized to other interfaces. For example, for the Si/ SiO_2 interface, the difference between the DFT and the experimental VBO is larger than 1 eV. Recent accurate calculations have shown that the QP corrections account for this discrepancy,³⁶ and hence they are essential to reproduce quantitatively the experimental measurements. For the Si/ ZrO_2 interface, a correction of about 1.1 eV has been extracted from *GW* calculations for Si³⁵ and ZrO_2 ⁴⁹ and used together with

the experimental band gap to correct DFT BOs in several works.^{14,15} For the Si/HfO₂ interface, the same correction as for Si/ZrO₂ has been adopted¹⁶ since there were no *GW* calculations available for HfO₂. Such an assumption seems quite reasonable given the analogous electronic structure of ZrO₂ and HfO₂. However, for both Si/ZrO₂ and Si/HfO₂ interfaces, the VBOs obtained applying this correction are too large (and as a consequence the CBOs too small) with respect to the available experiments.^{14,15,16}

In this work, the origin of this disagreement is discussed. QP calculations are performed for the thermodynamically stable phases (cubic, tetragonal and monoclinic) of HfO₂ and ZrO₂ as well for a strained tetragonal polymorph. In particular, we calculate the QP corrections at the top valence and bottom conduction bands in order to determine the fundamental band gaps and by comparison with Si, the QP correction for the Si/oxide band offsets. In contrast with previous QP calculations, our results show that the VBO remains almost unchanged while the CBO is corrected by 1.3–1.5 eV, thus explaining the success of the scissor-corrected DFT. The paper is organized as follows. In Sec. II, the methodological background is briefly described. Sec. III is devoted to the presentation and discussion of our results: the DFT geometries and band structures, the QP corrections to the band gaps, and finally the QP corrections to the Si/oxide band offsets.

II. METHODOLOGICAL BACKGROUND

The geometries and electronic structures for all the systems are computed within the DFT. All the calculations are carried out with the ABINIT³⁷ code within the LDA for the exchange–correlation energy functional.³⁸ Troullier-Martins³⁹ norm conserving pseudopotentials are used which include semicore states in the pseudopotentials for Zr and Hf (for details see Refs. 3,4). The wave functions are expanded on a plane-wave basis set up to kinetic energy cutoff of 12 Ha for Si and up to 30 Ha for the HfO₂ and ZrO₂ polymorphs. For all systems, the Brillouin zone (BZ) is sampled with a 4×4×4 Monkhorst–Pack⁴⁰ grid.

The QP energies are evaluated using the MBPT within the *GW* approximation. In this approach, the DFT eigenenergy E_n^{DFT} and wavefunction ψ_n^{DFT} for the n^{th} state are used as a zeroth-order approximation for their quasiparticle counterparts. Thus, the QP energy E_n^{QP} is calculated by adding to E_n^{DFT} the first-order perturbation correction that comes from replacing the DFT exchange–correlation potential $v_{\text{xc}}^{\text{DFT}}$ with the *GW* self-energy operator Σ_{GW} :

$$E_n^{\text{QP}} = E_n^{\text{DFT}} + \Re\{Z_n \langle \psi_n^{\text{DFT}} | \Sigma_{\text{GW}} - v_{\text{xc}}^{\text{DFT}} | \psi_n^{\text{DFT}} \rangle\}. \quad (1)$$

The renormalization factor Z_n accounts for the fact that Σ_{GW} , which is energy dependent, should be evaluated at E_n^{QP} . The *GW* self-energy operator Σ_{GW} writes as a

convolution in frequency space between the one-electron Green’s function G and the screened Coulomb potential W :

$$\Sigma_{\text{GW}}(\mathbf{r}, \mathbf{r}'; \omega) = \frac{i}{2\pi} \int d\omega' e^{i\delta\omega'} G(\mathbf{r}, \mathbf{r}'; \omega') W(\mathbf{r}, \mathbf{r}'; \omega - \omega'), \quad (2)$$

where δ is a positive infinitesimal. The explicit expression for the Green’s function G is:

$$G(\mathbf{r}, \mathbf{r}'; \omega) = \sum_n \frac{\psi_n^{\text{DFT}}(\mathbf{r}) [\psi_n^{\text{DFT}}(\mathbf{r}')]^*}{\omega - E_n^{\text{DFT}} + i\delta \text{sgn}(E_n^{\text{DFT}} - \mu)}, \quad (3)$$

where μ is the chemical potential. The screened Coulomb potential is determined as convolution between the inverse of the dielectric function ϵ^{-1} and the bare Coulomb interaction:

$$W(\mathbf{r}, \mathbf{r}'; \omega) = \int d\mathbf{r}'' \frac{\epsilon^{-1}(\mathbf{r}, \mathbf{r}''; \omega)}{|\mathbf{r}'' - \mathbf{r}'|}. \quad (4)$$

The dielectric function ϵ is calculated within the Random Phase Approximation. Its dependence on the frequency is approximated using the plasmon pole model (PPM) proposed by Godby and Needs.⁴¹ For the cubic ZrO₂, we explicitly test the validity of this choice. On the one hand, we perform the same calculation with the PPM proposed by Hybertsen and Louie.⁴² On the other hand, we take into account the full frequency dependence of the dielectric matrix without resorting to any PPM at all,^{43,44} in order to discriminate between the two PPMs.

In our QP calculations, both G [Eq. (3)] and W [Eq. (4)] are first evaluated from the DFT eigensolutions (which is often referred to as G_0W_0). Successively, the DFT energies are self-consistently replaced in Eq. (3) by the corrected values obtained from Eq. (1) (GW_0). The QP corrections are evaluated only for a few valence and conduction bands around the gap, the other energies E_n^{QP} are extrapolated using a scissor operator. We find that 2–3 iterations are enough to converge the orbital energies up to 0.01–0.02 eV. A systematic study⁴⁵ on several bulk systems has recently pointed out GW_0 as a practical and accurate method for evaluating QP energies. Indeed, while G_0W_0 provides underestimated energies for almost all systems, GW_0 shows a good agreement with both experimental data and full self-consistent *GW* including a Bethe–Salpeter-like vertex correction.⁴⁶

The *GW* calculations are performed with the YAMBO⁴⁷ code, except for the calculation of cubic ZrO₂ with the PPM of Hybertsen and Louie,⁴² which is performed with the ABINIT code. We carefully study the convergence of the QP corrections with the numerical cutoffs: for Si and the cubic polymorphs of HfO₂ and ZrO₂, we include 200 bands in the calculations of the Green’s function [Eq. (3)], and 200 bands and 331 reciprocal lattice vectors in the calculation of the dielectric matrix⁴⁸ in Eq. (4). For the tetragonal polymorphs (strained and at equilibrium), we include 500 bands in the calculations of the Green’s function, and 300 bands and 735 reciprocal lattice vectors in

the calculation of the dielectric matrix. Finally, the monoclinic polymorphs requires 600 bands for the Green's function, and 400 bands and 1177 reciprocal lattice vectors for the dielectric matrix. With these parameters, we estimate an error on the QP energies of about 0.05–0.1 eV depending on the system.

III. RESULTS

A. DFT geometries and band structures

For both ZrO_2 and HfO_2 , the three thermodynamically stable phases (cubic [c], tetragonal [t], and monoclinic [m]) are investigated. In addition, a strained [s] form of the tetragonal polymorph is also considered in which two sides are fixed to $a = a_{\text{Si}}/\sqrt{2}$ ($a_{\text{Si}}=5.40$ Å is the LDA theoretical lattice constant of Si) while all other degrees of freedom are relaxed. This last structure aims at simulating the effect of the epitaxial strain on the oxide in the MOSFET device.

The calculated equilibrium parameters describing these four geometries are reported in Table I. Our results agree within 1–2% with previous LDA^{11,12,49,50} and GGA^{15,16,51,52,53,54,55} results, as well as with experimental data.⁵⁶ For the strained polymorphs (s- ZrO_2 and s- HfO_2), a contraction is observed along the tetragonal direction c of about 2% compared to their fully relaxed tetragonal analogs (t- ZrO_2 and t- HfO_2). This is a direct consequence of fixing the lattice constant a in the basal plane (in fact, a is expanded by 7% and 5% in s- ZrO_2 and s- HfO_2 , respectively). As an indirect consequence, the internal parameter d_z becomes larger in the strained forms. For the latter structure, no direct meaningful comparison is possible with previous works in which epitaxial strained tetragonal polymorphs are also considered,^{15,16} since these rely on the GGA value for Si lattice constant.

The band structure calculated within the LDA are reported in brown in Fig. 1 for the cubic, tetragonal, strained, and monoclinic forms of ZrO_2 and HfO_2 . For ZrO_2 , the LDA band structures are in good agreement with those presented in Ref. 50. The band structures of HfO_2 are overall very similar to those of ZrO_2 , with the important exception of the cubic phase [Fig. 1(a)]. Indeed, while c- ZrO_2 shows an indirect minimum band gap from X (top of the valence band) to Γ (bottom of the conduction band) of 3.4 eV, c- HfO_2 has a direct band gap at X of 3.5 eV. The indirect X- Γ gap—that is the minimum gap in c- ZrO_2 —is slightly larger (3.7 eV).

In the tetragonal phase [Fig. 1(b)], the top valence band is almost flat along the ΓZ and $\text{X}\Gamma\text{M}$ directions. It actually presents several maxima (close to X at ~ 0.20 in the $\text{X}\Gamma$ direction and close to Γ at ~ 0.20 in the ΓM direction, in A and Z). The conduction band minimum is located at Γ . The resulting indirect band gap is 4 eV for both t- ZrO_2 and t- HfO_2 , respectively. The effect of the strain is to reduce the band gap to 2.5 eV for ZrO_2 , and to 3.1 eV for HfO_2 [Fig. 1(c)]. The effect is larger for s-

		ZrO_2			HfO_2		
c	a	5.011			5.273		
t	a c d_z	3.547	5.086	0.040	3.616	5.169	0.031
s	a c d_z	3.817	4.980	0.058	3.817	5.053	0.041
m	a b c	5.050	5.185	5.190	5.171	5.276	5.292
	γ	99.09°			99.27°		
	M	(0.2780 0.0416 0.2097)			(0.2778 0.0404 0.2059)		
	O_1	(0.0789 0.3527 0.3279)			(0.0799 0.3527 0.3277)		
	O_2	(0.4460 0.7594 0.4838)			(0.4462 0.7600 0.4857)		

TABLE I: Structural parameters of the thermodynamically stable phases (cubic [c], tetragonal [t], and monoclinic [m]) and of the strained [s] tetragonal structure (see text) of ZrO_2 and HfO_2 . The lattice constants (a , b , and c) are in expressed in Å, while the angle γ (between a and b) is given in degrees. For the tetragonal and strained forms, the internal parameter d_z is the displacement of the oxygen atoms with respect to their ideal cubic position in units of the lattice vector c . For the monoclinic polymorph, the internal coordinates for the metal ($M=\text{Zr}$ or Hf) and the two oxygen (O_1 and O_2) atoms are given in terms of lattice vectors.

ZrO_2 since it has the larger mismatch with the Si lattice constant. A similar reduction of the band gap resulting from the Si-epitaxial strain was also observed in previous works.^{15,16} For both s- ZrO_2 and s- HfO_2 , the valence band is almost flat along the $\text{X}\Gamma\text{M}$ direction. The maxima are located close to Γ , while the conduction band minimum is at Γ .

For the monoclinic phase [Fig. 1(d)], the top of the valence band is located at Γ while the bottom of the conduction band is located at B. The indirect minimum band gap is 3.7 eV and 3.8 eV for m- ZrO_2 and m- HfO_2 , respectively.

B. QP corrections on the band gaps

For all systems, the QP corrections are reported in Table II and the resulting band structures appear in black in Fig. 1. The effect of the QP corrections is to lower the valence bands and to raise the conduction bands. For both ZrO_2 and HfO_2 , the QP corrections on the band edges depend only weakly on the structure (c, t, s, or m). The correction δE_v at the valence band maximum (VBM) varies from -0.3 to -0.5 eV in ZrO_2 and from -0.4 to -0.5 eV in HfO_2 , while the correction δE_c at the conduction band minimum (CBM) ranges from 1.4 to 1.5 eV in ZrO_2 and from 1.5 to 1.7 eV in HfO_2 . Moreover, the QP corrections are not affecting the location of the minima and maxima found in the LDA bandstructures. The net effect of the QP corrections is thus to open the LDA band gaps by $\delta E_g = \delta E_c - \delta E_v$ varying from 1.8 to 2 eV for ZrO_2 and from 1.9 to 2.1 eV for HfO_2 . The difference between the ZrO_2 and HfO_2 band gaps found in LDA is increased by ~ 0.2 eV when including the QP

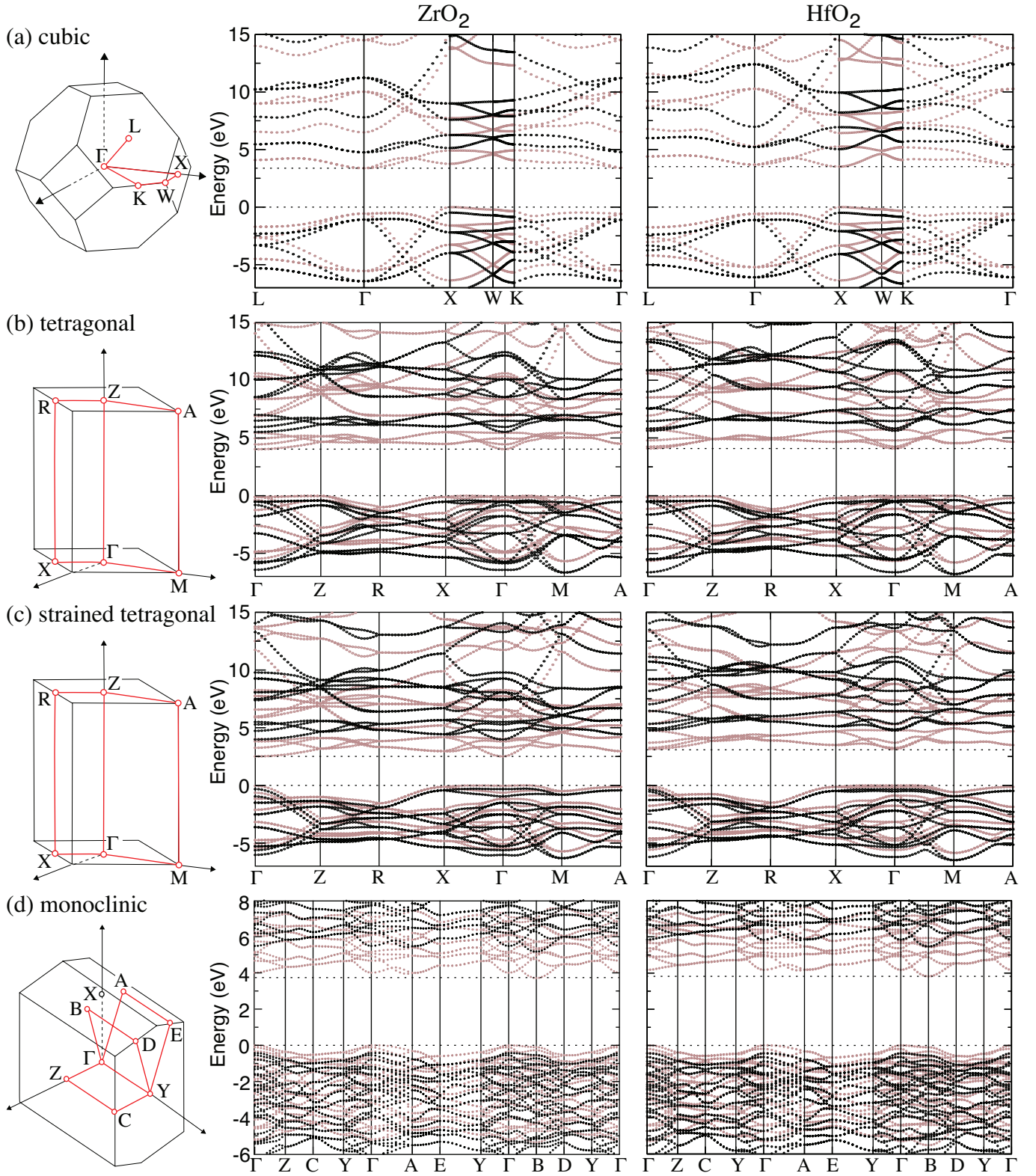


FIG. 1: [color online] Theoretical band structure within the LDA (brown circles) and GW_0 (black circles) along high symmetry axis of the BZ for the (a) cubic, (b) tetragonal, (c) strained, and (d) monoclinic phases of ZrO_2 and HfO_2 . The GW_0 band structures have been extrapolated from the calculated QP corrections using a linear fit.

corrections (from 0.1 to 0.3 eV in the cubic and monoclinic phase, from 0.6 to 0.8 eV in the strained phase), except for the tetragonal phase in which the band gaps differ by less than 0.1 eV both at the LDA and QP level.

	Si	ZrO ₂				HfO ₂			
		c	t	s	m	c	t	s	m
E_g^{DFT}	0.4	3.4	4.0	2.5	3.7	3.5	4.1	3.1	3.8
δE_v	-0.6	-0.5	-0.4	-0.3	-0.4	-0.5	-0.4	-0.4	-0.4
δE_c	0.1	1.4	1.5	1.5	1.5	1.5	1.5	1.6	1.7
E_g^{QP}	1.1	5.3	5.9	4.3	5.6	5.5	6.0	5.1	5.9

TABLE II: For bulk Si, and bulk ZrO₂ and HfO₂ in the cubic (c), tetragonal (t), monoclinic (m) phases and strained (s) polymorph: the minimum DFT band gap E_g^{DFT} , the minimum QP band gap E_g^{QP} at GW_0 level and the QP corrections δE_v and δE_c to the VBM and CBM, respectively.

For ZrO₂, the QP correction to the band gap, which is 1.9 eV in the three thermodynamically stable phase, is 0.4 eV lower than the value previously obtained in Ref. 49 for the cubic phase. This variation can be attributed to the different PPM (by Hybertsen Louie⁴²) used by the authors in the frequency integration of Eq. (4). Indeed, by repeating our calculation for the cubic phase with the same PPM, the QP correction to the band gap increases up to 2.4 eV in good agreement with Ref. 49. In order to discriminate between the two PPMs, the calculation is also repeated without resorting to any PPM. The QP correction is found to be 2.1 eV, which is 0.2 eV higher than the value obtained with the Godby and Needs PPM, and 0.3 eV lower than the one obtained with the Hybertsen and Louie PPM. It can be argued that our QP corrections to the band gap and hence the resulting QP band gaps are probably also underestimated for the other polymorphs of ZrO₂ and for HfO₂ due to the use of the PPM. Thus, when comparing the results with the experiments or other theoretical work, this extra uncertainty of about 0.2 eV should also be taken into account.

Our calculated QP band gaps for c-, t-, and m-ZrO₂, also show an overall agreement with those of Ref. 57 relying on the screened-exchange LDA method. This confirms the validity of this approximation for the calculation of band structures. For HfO₂, our result for the cubic phase agrees well with the GW band gap reported in Ref. 58, while for the tetragonal and monoclinic phase our values are larger by 0.2 eV.

Experimentally, the optical band gaps determined from energy loss and transmission spectroscopies range from 5.2 to 5.7 eV for ZrO₂^{31,50,59,60,61,62,63} and from 5.3 to 5.8 eV for HfO₂^{31,64,65,66,67}. Hence, the agreement between our calculations of the fundamental gap and experimental results is quite reasonable considering the temperature, excitonic, and impurities effects and the possible substrate strain in case of deposited films that should be taken into account. For the thermodynamically stable phases of ZrO₂, reflectance vacuum ultraviolet spec-

troscopy indicate 6.1–7.1 eV, 5.8–6.6 eV, and 5.8–7.1 eV for the cubic, tetragonal, and monoclinic phases, respectively. For the last two, our calculated values fall into the range of the experimental estimates. In contrast, for the cubic phase, our band gap is much lower even when considering the minimum direct band gap (5.5 eV at X) and when taking into account the underestimation by 0.2 eV coming from the PPM. This discrepancy may be related to the yttrium used to stabilize the cubic phase at room temperature and/or the tendency of reflectance measurements to overestimate the gap (see Ref. 50 for a thorough discussion). For HfO₂, a “theoretical” band gap of 6.7 eV⁶⁸ was proposed for a film deposited on a SiO_xN_y/p-Si substrate (monoclinic phase) by comparing direct/inverse photoemission spectroscopy with DFT density-of-states calculations, arguing that the reduction of 0.9 eV with respect to the experimental band gap (5.9 eV) should be attributed to defects tail states. Our value compares better with the band gap determined directly from the experiment.

C. QP corrections on the Si/oxide band offsets

In the DFT approach, the VBO and CBO are conveniently split into two terms:

$$\text{VBO} = \Delta E_v^{\text{DFT}} + \Delta V \quad (5)$$

$$\text{CBO} = \Delta E_c^{\text{DFT}} + \Delta V \quad (6)$$

The first term ΔE_v^{DFT} [resp. ΔE_c^{DFT}] on the right-hand side of Eq. (5) [resp. Eq. (6)] is referred to as the *band-structure contribution*. It is defined as the difference between the VBM [resp. the CBM] *relative to the average of the electrostatic potential in each material*. These are obtained from two independent standard bulk calculations on the two interface materials. The second term ΔV , called the *lineup of the average of the electrostatic potential* across the interface, accounts for all the intrinsic interface effects. It is determined from a supercell calculation with a model interface.

Despite the DFT limitations in finding accurate eigenenergies, the VBOs are often obtained with a very good precision, in particular for semiconductors.²² This has opened an indirect route to compute the CBOs through the experimental band gaps using:

$$\text{CBO} = \Delta E_g^{\text{exp}} + \text{VBO} \quad (7)$$

where ΔE_g^{exp} is the difference between the experimental values of the band gap of each material. Note that this equation is equivalent to applying a scissor correction to the conduction bands on both sides of the interface, as can be seen by inserting Eq. (5) in Eq. (7):

$$\text{CBO} = \Delta E_c^{\text{DFT}} + \Delta V + (\Delta E_g^{\text{exp}} - \Delta E_g^{\text{DFT}}) \quad (8)$$

and comparing with Eq. (6).

As discussed in the introduction, this scissor-corrected DFT scheme has been used in several studies of the

Si/ZrO₂ and Si/HfO₂.^{9,10,11,12} For the stable insulating O-terminated interfaces of Si/ZrO₂ and Si/HfO₂, the VBOs calculated are found to range from 2.5 to 3 eV, in good agreement with the experimental findings (2.7–3.4 eV).^{23,24,25,26,27,28,29,30,31} Adopting $\Delta E_g^{\text{exp}}=4.7$ eV ($E_g^{\text{exp}}=1.1$ eV for Si and 5.8 eV for ZrO₂ and HfO₂) in Eq. (8), the scissor-corrected CBOs lie thus between 1.7 and 2.2 eV. This is also in good agreement with experiments (1.5–2.0 eV).^{28,29,30,31}

In the QP framework, it was often assumed³⁵ and it has recently been proven³⁶ that the lineup of the potential ΔV is already well-described within DFT. So that, only the band-structure contribution is modified:

$$\text{VBO} = \Delta E_v^{\text{QP}} + \Delta V = \Delta E_v^{\text{DFT}} + \Delta(\delta E_v) + \Delta V \quad (9)$$

$$\text{CBO} = \Delta E_c^{\text{QP}} + \Delta V = \Delta E_c^{\text{DFT}} + \Delta(\delta E_c) + \Delta V \quad (10)$$

where $\delta E_v = E_v^{\text{QP}} - E_v^{\text{DFT}}$ (resp. $\delta E_c = E_c^{\text{QP}} - E_c^{\text{DFT}}$) is the quasiparticle correction at the VBM (resp. CBM) and $\Delta(\delta E_v)$ [resp. $\Delta(\delta E_c)$] is the corresponding difference between the two materials.

For the Si/ZrO₂ and Si/HfO₂ interfaces, no specific *GW* study exists as such. However, Fiorentini *et al.*¹⁴ evaluated the QP effects on the VBO of Si/ZrO₂ combining the value for tetragonal ZrO₂ ($\delta E_v=-1.23$ eV) from Ref. 49 with the value for Si from Ref. 35 ($\delta E_v=-0.15$ eV). This results in a total correction of $\Delta(\delta E_v)=1.08$ eV on the VBO in Eq. (9). This value has been used in several other works,^{15,16} even for Si/HfO₂ interfaces. For both Si/ZrO₂ and Si/HfO₂ interfaces, the VBOs obtained in this way were found to be too large (and as a consequence the CBOs too small) with respect to the experimental values.^{14,15,16}

For the oxides, our QP corrections to the DFT valence band δE_v vary from -0.3 to -0.5 eV; while for the conduction bands, δE_c ranges from 1.4 to 1.7 eV. For Si, our QP corrections, which are reported in Table II, lead to a band gap that agrees well with previous theoretical works (e.g. see Ref. 45), and with the experimental value.⁶⁹ The total QP correction to the gap δE_g of about 0.7 eV, comes mostly from the downshift of valence band state ($\delta E_v=-0.6$ eV). This δE_v value is almost the same as that found for the polymorphs of both ZrO₂ and HfO₂. Therefore, the QP correction on the VBOs are only of 0.1–0.2 eV and the correction on the CBOs is about 1.3–1.5 eV. This explains why previous studies based on scissor-corrected DFT were in such a good agreement with experimental results.

Turning to previous works^{14,15,16} that accounted for QP corrections to the BOs of Si/ZrO₂ and Si/HfO₂ interfaces using values from prior *GW* calculations,^{35,49} their disagreement with experiments can be explained as follows. On the one hand, the QP corrections in the oxide and Si are not consistent since a different approximation has been used in Eq. (4) for the dielectric function ϵ . The calculations for Si use a model dielectric function,³⁵ while the calculations for ZrO₂ use the Random Phase Approximation. In particular, the value obtained for Si $\delta E_v=-0.2$ eV is lower in absolute value with respect to

the value found from the Random Phase Approximation ($\delta E_v=-0.6$ eV), and hence this inconsistency artificially increases the QP correction on the VBO. On the other hand, our QP results (in particular, those for c- and t-ZrO₂) differ from those obtained in Ref. 49 where it was found that the total QP correction $\delta E_g=2.3$ eV resulted from lowering the valence bands by about 1.3 eV, and raising the conduction band by about 1.1 eV. The difference with our results is due again to the different PPM used. Indeed, repeating the calculations with the Hybertsen and Louie PPM for the cubic phase, we found a correction δE_v of -1.1 eV for the valence and δE_c of $+1.3$ eV for the conduction in agreement with Ref. 49. When performing the same calculation without resorting to any PPM, we obtain $\delta E_v=-0.7$ eV and $\delta E_c=1.4$ eV, meaning that δE_v is 0.2 eV too low for the Godby and Needs PPM, and 0.5 eV too high for the Hybertsen and Louie PPM. For the conduction bands, δE_c differs by less than 0.1 eV with the former, while it is 0.3 eV too low with the latter.

As final remark, we stress that rigorously, the QP corrections on the band offsets should be calculated using the same pseudopotential and the same exchange-correlation approximation as for the interface calculations. Indeed, while the *GW* band gap has been demonstrated to be quite insensitive to the starting point, this is not true for the QP corrections that reflect—as a consequence—the differences in the choice of the pseudopotential and the exchange-correlation approximation. Therefore, we would recommend to calculate—when possible—QP corrections on DFT band offsets using the same pseudopotentials, and exchange-correlation approximation as for the interface calculation and using the same PPM for both materials.

IV. SUMMARY

The electronic properties of ZrO₂ and HfO₂ polymorphs and their interface with Si have been investigated using *GW* calculations. The QP corrections are found to be very similar for the two oxides consistently with their analogous band structure, and depend only slightly on the crystalline structure. While, at the DFT level, the epitaxial strain was found to dramatically shrink the band gap (especially for ZrO₂ for which the lattice parameter mismatch with Si is larger), the QP corrections depend only slightly on the strain. When considering the interface Si/oxide, the QP corrections to the VBOs were calculated to be very small (a few tenths of eV) by cancellation of the corrections on the valence band maximum of the Si and those of oxides. On the other hand, the correction was found to be of the order of 1.5 eV for the CBOs. These results disagree with the correction on the VBOs of more than 1 eV used in the literature,^{14,15,16} which was extracted from existing *GW* calculations.^{35,49} We have traced back the differences with our results to the difference in the PPM used for the ZrO₂, and to

the inconsistency in the level of approximation for the screened interaction W . Our results combined with the DFT band offsets available from the literature for different interfacial bonding models provide values in a good agreement with the experiment.

Acknowledgments

M.G. thanks Dr. Andrea Marini for his precious support for the use of the YAMBO code. The au-

thors acknowledge useful discussion with Dr. Matteo Giantomassi, Dr. Patrick Rinke, Dr. Alberto Zobelli, Dr. Geoffrey Pourtois and Prof. Michel Houssa. This work was supported by the EU's Sixth and Seventh Framework Programs through the Nanoquanta Network of Excellence (NMP4-CT-2004-50019), the ETSF I3 e-Infrastructure project (Grant Agreement 211956), and the project FRFC N°. 2.4502.05. G.M.R. acknowledges the FNRS of Belgium for financial support.

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- ¹ G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.* **89**, 5243 (2001).
 - ² See e.g. URL <http://tinyurl.com/high-k-intel>, URL <http://tinyurl.com/high-k-ibm>, URL <http://tinyurl.com/high-k-nec>.
 - ³ G. M. Rignanese, F. Detraux, X. Gonze, and A. Pasquarello, *Phys. Rev. B* **64**, 134301 (2001).
 - ⁴ G. M. Rignanese, X. Gonze, G. Jun, K. J. Cho, and A. Pasquarello, *Phys. Rev. B* **69**, 184301 (2004).
 - ⁵ G. M. Rignanese, X. Gonze, G. C. Jun, K. J. Cho, and A. Pasquarello, *Phys. Rev. B* **70**, 099903(E) (2004).
 - ⁶ M. Peressi, N. Binggeli, and A. Baldereschi, *J. Phys. D Appl. Phys.* **31**, 1273 (1998).
 - ⁷ S. Q. Wang and H. Q. Ye, *Curr. Opin. Solid St. M.* **10**, 26 (2006).
 - ⁸ A. A. Demkov, O. Sharia, X. H. Luo, and J. Lee, *Microelectron. Reliab.* **47**, 686 (2007).
 - ⁹ P. W. Peacock and J. Robertson, *Phys. Rev. Lett.* **92**, 057601 (2004).
 - ¹⁰ P. W. Peacock, K. Xiong, K. Y. Tse, and J. Robertson, *Phys. Rev. B* **73**, 075328 (2006).
 - ¹¹ R. Puthenkovilakam, E. A. Carter, and J. P. Chang, *Phys. Rev. B* **69**, 155329 (2004).
 - ¹² R. Puthenkovilakam and J. P. Chang, *J. Appl. Phys.* **96**, 2701 (2004).
 - ¹³ G. H. Chen, Z. F. Hou, and X. G. Gong, *Appl. Phys. Lett.* **95**, 102905 (2009).
 - ¹⁴ V. Fiorentini and G. Gulleri, *Phys. Rev. Lett.* **89**, 266101 (2002).
 - ¹⁵ Y. F. Dong, Y. P. Feng, S. J. Wang, and A. C. H. Huan, *Phys. Rev. B* **72**, 045327 (2005).
 - ¹⁶ B. R. Tuttle, C. Tang, and R. Ramprasad, *Phys. Rev. B* **75**, 235324 (2007).
 - ¹⁷ J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983).
 - ¹⁸ L. J. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**, 1888 (1983).
 - ¹⁹ M. Grüning, A. Marini, and A. Rubio, *J. Chem. Phys.* **124**, 154108 (2006).
 - ²⁰ M. Grüning, A. Marini, and A. Rubio, *Phys. Rev. B* **74**, 161103(R) (2006).
 - ²¹ Recently hybrid DFT methods combining nonlocal approximations for the exchange–correlation potential, such as the screened exchange, with local density or generalized gradient approximations, have been shown to provide sensible results for the bandgap of semiconductors and covalent insulators and could be a promising approach to calculate band offsets. See e.g. J. Heyd, and G. Scuseria *J. Chem. Phys.* **121**, 1187 (2004).
 - ²² C. G. Van de Walle and R. M. Martin, *Phys. Rev. B* **35**, 8154 (1987).
 - ²³ S. Miyazaki, M. Narasaki, M. Ogasawara, and M. Hirose, *Microelectron. Eng.* **59**, 373 (2001).
 - ²⁴ M. Oshima, S. Toyoda, T. Okumura, J. Okabayashi, H. Kumigashira, K. Ono, M. Niwa, K. Usuda, and N. Hirashita, *Appl. Phys. Lett.* **83**, 2172 (2003).
 - ²⁵ S. J. Wang, A. C. H. Huan, Y. L. Foo, J. W. Chai, J. S. Pan, Q. Li, Y. F. Dong, Y. P. Feng, and C. K. Ong, *Appl. Phys. Lett.* **85**, 4418 (2004).
 - ²⁶ G. B. Rayner, D. Kang, Y. Zhang, and G. Lucovsky, *J. Vac. Sci. Technol. B* **20**, 1748 (2002).
 - ²⁷ S. Sayan, E. Garfunkel, and S. Suzer, *Appl. Phys. Lett.* **80**, 2135 (2002).
 - ²⁸ S. Sayan, R. A. Bartynski, X. Zhao, E. P. Gusev, A. Vanderbilt, M. Croft, M. B. Holl, and E. Garfunkel, *Phys. Status Solidi B* **241**, 2246 (2004).
 - ²⁹ V. V. Afanas'ev, A. Stesmans, F. Chen, X. Shi, and S. A. Campbell, *Appl. Phys. Lett.* **81**, 1053 (2002).
 - ³⁰ O. Renault, N. T. Barrett, D. Samour, and S. Quiaia-Marthon, *Surf. Sci.* **566**, 526 (2004).
 - ³¹ E. Bersch, S. Rangan, R. A. Bartynski, E. Garfunkel, and E. Vescovo, *Phys. Rev. B* **78**, 085114 (2008).
 - ³² F. Aryasetiawan and O. Gunnarsson, *Rep. Progr. Phys.* **61**, 237 (1998).
 - ³³ L. Hedin, *J. Phys.: Condens. Matter* **11**, R489 (1999).
 - ³⁴ W. G. Aulbur, L. Jonsson, and J. W. Wilkins, *Solid State Phys.* **54**, 1 (2000).
 - ³⁵ X. J. Zhu and S. G. Louie, *Phys. Rev. B* **43**, 14142 (1991).
 - ³⁶ R. Shaltaf, G. M. Rignanese, X. Gonze, F. Giustino, and A. Pasquarello, *Phys. Rev. Lett.* **100**, 186401 (2008).
 - ³⁷ X. Gonze, J. M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G. M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, *et al.*, *Comp. Mater. Sci.* **25**, 478 (2002); X. Gonze, G. M. Rignanese, M. Verstraete, J. M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, *et al.*, *Z. Kristallogr.* **220**, 558 (2005).
 - ³⁸ D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
 - ³⁹ N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).

- (1991).
- ⁴⁰ H. Monkhorst and J. Pack, Phys. Rev. B **13**, 5188 (1976).
 - ⁴¹ R. W. Godby and R. J. Needs, Phys. Rev. Lett. **62**, 1169 (1989),
 - ⁴² M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
 - ⁴³ A. Marini, G. Onida and R. Del Sole, Phys. Rev. Lett. **88**, 016403 (2001).
 - ⁴⁴ A. Marini, Ph.D. Thesis, Università Rome Tor Vergata, Rome, 2001.
 - ⁴⁵ M. Shishkin and G. Kresse, Phys. Rev. B **75**, 235102 (2007).
 - ⁴⁶ M. Shishkin, M. Marsman, and G. Kresse, Phys. Rev. Lett. **99**, 246403 (2007).
 - ⁴⁷ A. Marini, C. Hogan, M. Grüning and D. Varsano, Comp. Phys. Comm. **180**, 1392 (2009).
 - ⁴⁸ For the calculation without the PPM, the inverse dielectric matrix is computed explicitly for 100 frequencies ranging from 1 to 230 eV, and the integration in Eq. (4) performed numerically.
 - ⁴⁹ B. Kralik, E. K. Chang, and S. G. Louie, Phys. Rev. B **57**, 7027 (1998).
 - ⁵⁰ L. K. Dash, N. Vast, P. Baranek, M. C. Cheynet, and L. Reining, Phys. Rev. B **70**, 245116 (2004).
 - ⁵¹ A. S. Foster, V. B. Sulimov, F. LopezGejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B **64**, 224108 (2001).
 - ⁵² J. E. Jaffe, R. A. Bachorz, and M. Gutowski, Phys. Rev. B **72**, 144107 (2005).
 - ⁵³ R. Terki, H. Feraoun, G. Bertrand, and H. Aourag, Comp. Mater. Sci. **33**, 44 (2005).
 - ⁵⁴ A. B. Mukhopadhyay, J. F. Sanz, and C. B. Musgrave, Phys. Rev. B **73**, 115330 (2006).
 - ⁵⁵ J. C. Garcia, L. M. R. Scolfaro, A. T. Lino, V. N. Freire, G. A. Farias, C. C. Silva, H. W. L. Alves, S. C. P. Rodrigues, and E. F. da Silva, J. Appl. Phys. **100**, 104103 (2006).
 - ⁵⁶ See references to experimental data in Refs. 50,54
 - ⁵⁷ J. E. Medvedeva, A. J. Freeman, C. B. Geller, and D. M. Rishel, Phys. Rev. B **76**, 235115 (2007).
 - ⁵⁸ K. Nishitani, P. Rinke, P. Eggert, S. J. Hashemifar, P. Kratzer, and M. Scheffler, as reported by Cheynet *et al.* J. Appl. Phys. **101**, 054101 (2007).
 - ⁵⁹ R. H. French, S. J. Glass, F. S. Ohuchi, Y. N. Xu, and W. Y. Ching, Phys. Rev. B **49**, 5133 (1994).
 - ⁶⁰ C. R. Aita, E. E. Hoppe, and R. S. Sorbello, Appl. Phys. Lett. **82**, 677 (2003).
 - ⁶¹ H. Nohira, W. Tsai, W. Besling, E. Young, J. Petry, T. Conard, W. Vandervorst, S. De Gendt, M. Heyns, J. Maes, *et al.*, J. Non-Cryst. Solids **303**, 83 (2002).
 - ⁶² I. Kosacki, V. Petrovsky, and H. U. Anderson, Appl. Phys. Lett. **74**, 341 (1999).
 - ⁶³ S. Sayan, N. V. Nguyen, J. Ehrstein, T. Emge, E. Garfunkel, M. Croft, X. Y. Zhao, D. Vanderbilt, I. Levin, E. P. Gusev, *et al.*, Appl. Phys. Lett. **86**, 152902 (2005).
 - ⁶⁴ M. C. Cheynet, S. Pokrant, F. D. Tichelaar, and J. L. Rouviere, J. Appl. Phys. **101**, 054101 (2007).
 - ⁶⁵ T. V. Perevalov, V. A. Gritsenko, S. B. Erenburg, A. M. Badalyan, H. Wong, and C. W. Kim, J. Appl. Phys. **101**, 053704 (2007).
 - ⁶⁶ H. Y. Yu, M. F. Li, B. J. Cho, C. C. Yeo, M. S. Joo, D. L. Kwong, J. S. Pan, C. H. Ang, J. Z. Zheng, and S. Ramanathan, Appl. Phys. Lett. **81**, 376 (2002).
 - ⁶⁷ M. Balog, M. Schieber, M. Michman, and S. Patai, Thin Solid Films **41**, 247 (1977).
 - ⁶⁸ S. Sayan, T. Emge, E. Garfunkel, X. Y. Zhao, L. Wielunski, R. A. Bartynski, D. Vanderbilt, J. S. Suehle, S. Suzer, and M. Banaszak-Holl, J. Appl. Phys. **96**, 7485 (2004).
 - ⁶⁹ J. E. Ortega and F. J. Himpsel, Phys. Rev. B **47**, 2130 (1993).